STFD.021C1
January 7, 2002

CARBON NANOTUBE STRUCTURE HAVING A CATALYST ISLAND

INSA1 >

Related Patent Documents

This is a continuation of U.S. Patent Application Serial No. 09/133,948 (STFD.021PA/S98-049) filed on August 14, 1998 and entitled "Carbon Nanotube Structures made Using Catalyst Islands," to which priority is claimed under 35 U.S.C. §120 for common subject matter and which is fully incorporated herein by reference.

Field of the Invention

The present invention relates generally to carbon nanotubes and more particularly to the growth of carbon nanotubes using catalyst islands.

Background

Carbon nanotubes including single-walled carbon nanotubes (SWNT) are ideal quantum systems for exploring basic science in one-dimension. These novel molecular-scale wires, derived by bottom-up chemical synthesis approaches are also promising as core components or interconnecting wires for electronics and other applications. Rich quantum phenomena have been revealed with SWNTs and functional electronic devices such as transistors, chemical sensors and memory devices have been built. In these and other devices, it is sometimes desirable to use individual, high quality SWNTs.

Obtaining individual, high quality, single-walled nanotubes has proven to be a difficult task, particularly when manufacturing the nanotubes in bulk quantities. Previous methods for the production of nanotubes yield bulk materials with tangled

nanotubes. Nanotubes in such bulk materials are typically in a bundled form. These tangled nanotubes are difficult to purify, isolate, manipulate, and use as discrete elements for making functional devices. For example, in making functional microscopic devices, bulk tangled nanotubes are difficult to implement due to the difficulty of isolating one individual tube from the tangled nanotubes, manipulating the tube, and constructing a functional device using the isolated tube. Also, carbon nanotubes manufactured in this manner tend to exhibit molecular-level structural defects that result in weaker tubes with poor electrical characteristics. These and other difficulties have presented challenges to the manufacture of carbon nanotubes for implementation in a variety of applications, such as functional microscopic devices.

Summary of the Invention

The present invention is directed to carbon nanotubes and the fabrication thereof. The present invention is exemplified in a number of implementations and applications, some of which are summarized below.

In one example embodiment of the present invention, an individual, distinct nanotube device includes a catalyst island and a nanotube extending therefrom. In one implementation, the nanotube is a single-walled carbon nanotube. The nanotube device is adapted to be implemented in one or more semiconductor microstructures.

In one implementation, the catalyst island is located on a top surface of a semiconductor substrate, which may, for example, include silicon, alumina, quartz, silicon oxide or silicon nitride. The catalyst may include Fe_2O_3 or other catalyst

materials including molybdenum, cobalt, nickel, or zinc and oxides thereof. In one implementation, the catalyst island is between about 1 and 5 microns in size.

In another example embodiment of the present invention, individual, distinct single-walled nanotubes are grown from catalyst islands. The nanotubes are grown using a hydrocarbon gas that is introduced to the catalyst islands, where the hydrocarbon gas is reacted. The nanotube growth is confined to selected locations, and the resulting nanotubes can be easily addressed and integrated into structures to obtain functional microscopic devices.

In another example embodiment of the present invention, a nanotube-tipped atomic force microscope (AFM) device includes a nanotube extending from a catalyst island on a cantilever tip. The cantilever is adapted for use as a scanning tip in conventional AFM applications.

In another example embodiment of the present invention, a carbon nanotube device includes a substrate with two electrically conductive catalyst islands coupled to one another by a nanotube extending between the islands. The nanotube and the catalyst island are adapted for electrically coupling to other circuitry, such as via a conductive interconnect. In one implementation, the nanotube is freestanding above the substrate and adapted for use as a high frequency, high-Q resonator. In another implementation, one of the catalyst islands is replaced by a conductive metal pad.

The above summary of the present invention is not intended to describe each illustrated embodiment or every implementation of the present invention. The figures and detailed description that follow more particularly exemplify these embodiments.

Brief Description of the Drawings

The invention may be more completely understood in consideration of the detailed description of various embodiments of the invention that follows in connection with the accompanying drawings, in which:

FIG. 1 shows a first step in making nanotubes, according to an example embodiment of the present invention;

FIG. 2 shows a second step in making nanotubes, according to another example embodiment of the present invention;

FIG. 3 shows a third step in making nanotubes, according to another example embodiment of the present invention;

FIG. 4 shows a top view of a substrate with three catalyst islands, according to another example embodiment of the present invention;

FIG. 5 shows a top view of a single catalyst island that has been used to grow nanotubes, according to another example embodiment of the present invention;

FIG. 6 shows an apparatus that has a nanotube connected between a catalyst island and a metal pad, according to another example embodiment of the present invention;

FIG. 7 shows metal covers disposed on top of catalyst islands and portions of nanotubes, according to another example embodiment of the present invention;

FIGs. 8A-8C illustrate the metal covers, such as those of FIG. 7, being made according to another example embodiment of the present invention;

FIG. 9 shows a side view of a resonator made from a freestanding nanotube supported by the ends of the nanotube, according to another example embodiment of the present invention;

FIG. 10 shows a top view illustrating a carbon nanotube device, such as that shown in FIG. 9, being made according to another example embodiment of the present invention;

FIGs. 11A and 11B illustrate a method of making a carbon nanotube device, such as that shown in FIG. 9, according to another example embodiment of the present invention;

FIG. 12 shows an atomic force microscope tip undergoing manufacture, according to another example embodiment of the present invention; and

FIGs. 13A-13D illustrate a method of producing a carbon nanotube on a tip of an atomic force microscope cantilever, according to another example embodiment of the present invention.

While the invention is amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention.

Detailed Description

The present invention is believed to be applicable to a variety of different devices and implementations, and the invention has been found to be particularly suited for manufacturing carbon nanotubes. While the present invention is not necessarily limited to such applications, various aspects of the invention may be appreciated through a discussion of various examples using this context.

According to an example embodiment of the present invention, a carbon nanotube device includes a single-walled carbon nanotube extending from a catalyst particle. The particle may, for example, be located on a surface, such as a top surface of a semiconductor substrate or on a cantilever tip of an AFM. In one implementation, the carbon nanotube device includes a plurality of catalyst islands on a top surface of a substrate, each island having a carbon nanotube extending therefrom.

FIGs. 1-5 show individually distinct carbon nanotubes being grown, according to another example embodiment of the present invention. In FIG. 1, a layer of resist 20 is disposed and patterned on a top surface of a substrate 22 using, for example, electron beam (e-beam) lithography. The substrate 22 is made of material that may, for example, include one or more of silicon, alumina, quartz, silicon oxide or silicon nitride, and in one implementation, includes a metal film on the top surface. The patterning results in at least one hole 24 in the resist 20 that exposes the underlying substrate 22. In one implementation, holes formed in the resist are about 3-5 microns in size and are spaced apart by a distance 26 of about 10 microns.

In FIG. 2, a catalyst layer 28 is deposited on the surfaces of the resist 20 and substrate 22. The catalyst layer may include one or more of a variety of catalysts. In

one implementation, the catalyst includes a solution of $Fe(NO_3)_3$ in methanol, mixed with alumina nanoparticles having a diameter of about 15-30 nanometers. In other implementations, the catalyst includes one or more of: elemental metals; oxides of elemental metals (*e.g.*, iron, molybdenum and zinc oxides); a mixture of iron, molybdenum and ruthenium oxides; and iron salts such as Fe(SO4).

The nanoparticles can be made of many ceramic materials, depending upon the application and available materials. For instance, one or more of refractory oxide ceramic materials such as alumina and silica can be used. In one particular application using $Fe(NO_3)_3$, the catalyst preparation includes mixing 4.0 grams of alumina nanoparticles with 1.0 gram of $Fe(NO_3)*9H_2O$ in 30mL methanol for 24 hours. The mixture is applied to the substrate and the methanol is evaporated, leaving a layer 28 of alumina nanoparticles coated with $Fe(NO_3)_3$ adhering to the resist and in the holes 24. In FIG. 3, a lift-off process is performed, leaving isolated islands 29 of catalyst (*e.g.*, $Fe(NO_3)_3$-coated nanoparticles) adhering in regions where holes 24 existed. FIG. 4 shows a top view of the catalyst islands 29.

The substrate 22 is heated and nanoparticles of the catalyst are decomposed (*e.g.*, the $Fe(NO_3)_3$ is decomposed to Fe_2O_3). The substrate may be heated, for example, by placing the substrate in a furnace with an Argon atmosphere and heating to between about 100-400 degrees Celsius. The decomposed catalyst nanoparticles are an active catalyst that catalyzes the formation of carbon nanotubes when exposed to methane gas at elevated temperature.

In a more particular example embodiment of the present invention, the substrate with catalyst islands 29 is heated in a furnace at about 850-1000 degrees Celsius, and

99.99% pure methane is flowed over the catalyst islands 29 at a velocity of about 2-20 centimeters per second to grow single-walled nanotubes. In one implementation, a 1-inch diameter tube is used, wherein methane is introduced at a flow rate of about 600-6000cm^3/min to achieve a velocity of about 2-20 centimeters per second. The amount of time that the methane is introduced to the catalyst island is sufficient to react the methane and grow a nanotube, and in one implementation, is about 10 minutes.

The nanotubes are formed substantially straight and without structural flaws (*e.g.*, all the carbon rings in the nanotubes have 6 carbon atoms instead of 5 or 7 carbon atoms). Most of the nanotubes are single-walled, with diameters in the range of about 1-5 nanometers. At a furnace temperature of about 1000 degrees Celsius, it has been discovered that about 90% of the nanotubes are single-walled when grown. At a furnace temperature of about 900 degrees Celsius, about 99% of the tubes are single-walled with most of the nanotubes having diameters in the range of about 1-2 nanometers. The nanotubes have large length to diameter aspect ratios (*e.g.*, approaching about 10,000) and are very straight, due to the absence of structural flaws.

In another example embodiment of the present invention, nanoparticles are not used in forming the catalyst. Small quantities of Iron salts are deposited on the substrate (*e.g.*, by dissolving the iron salts in a solvent and evaporating the solvent), and the substrate is heated to decompose the iron salts without necessarily mixing the iron salts with nanoparticles.

In another example embodiment of the present invention, a furnace chamber is configured and arranged for manufacturing carbon nanotubes. The furnace is adapted to flow a carbon feedstock gas, such as methane, and to react the carbon feedstock gas

using a catalyst for growing carbon nanotubes. In one implementation, the furnace chamber is adapted to heat a substrate and catalyst to between about 850 and 1000 degrees Celsius, and to flow methane gas at a velocity of about 2-20 centimeters per second to a catalyst in the furnace. The methane may, for example, be reacted at catalyst islands on a substrate to form a carbon nanotube.

FIG. 5 shows a top view of the catalyst island 29 having a plurality of nanotubes 30 grown therefrom in random directions. The carbon nanotubes are disposed in contact with the substrate surface and are firmly attached to the island 29. The nanotubes are grown in a base-growth mode, where new carbon is added to the nanotubes 30 at the point where they are attached to the island 29, such that an end of the nanotubes that is opposite the end attached to the island is free. In one implementation, the nanotubes are adapted to be used as resonators wherein the free end vibrates.

In another example embodiment of the present invention, the carbon nanotubes 30 are not tangled together, are individually separable and are spaced apart by a substantial distance. In one implementation, between about 10-50 nanotubes are grown from a catalyst island. The individually separable nanotubes are particularly useful for the manufacture of electronic and micromechanical devices, wherein individual nanotubes are incorporated into the devices by appropriately locating islands 29. Electrical and mechanical connections are easily made to individual nanotubes if they are spatially separated and distinct.

In another example embodiment of the present invention, larger numbers of nanotubes are grown (*e.g.*, using a more effective catalyst). The nanotubes grown in

large numbers form bundles that are useful for many electrical and mechanical devices such as field effect transistors, single electron transistors, and resonators that have only one fixed end.

FIG. 6 is a top view of an electronic device made by locating the island 29 close to a patterned metal pad 32, according to another example embodiment of the present invention. A single nanotube 30a is grown extending from the island 29 to the metal pad 32 and electrically connecting the island 29 and pad 32. The island 29 and pad 32 are spaced apart by a distance in the range of between about 100 nanometers and 5 microns, with the likelihood that the nanotube grows to the pad 32 increasing as the distance between the pad 32 and island 29 is reduced. The island 29 and pad 32 are both electrically conductive, and a patterned conductive line 33 on the substrate surface electrically connects to the nanotube 30a on a macroscopic scale. The nanotube 30a with such a macroscopic electrical connection on each end can be used in many devices including field-effect transistors, single electron transistors and low current value fuses. In one implementation, the conductive line 33 is applied to the substrate 20 before the island 29 is deposited, such that the island rests on top of the conductive line 33. In another implementation, the conductive line 33 is disposed on top of the islands.

In another implementation (not shown), when two or more nanotubes simultaneously electrically connect the island 29 and metal pad 32, all but one of the nanotubes is broken with an AFM tip. For instance, an AFM tip can be dragged across the substrate surface so that it bends unwanted nanotubes until they break.

In another example embodiment of the present invention, a second catalyst island is substituted for the metal pad 32. In this implementation, the nanotube 30a

provides electrical contact between two catalyst islands instead of between the island 29 and the metal pad 32. Metal line 33 similarly provides electrical connection to the substituted catalyst island.

FIG. 7 shows a side view of a substrate 22 in which a metal cover 34 is deposited on top of each catalyst island 29, according to another example embodiment of the present invention. The metal covers 34 include one or more of a variety of metals, such as platinum or titanium-gold alloy. Each metal cover 34 covers a portion of each island 29 and covers an end portion 37 of the nanotube 30a and holds the nanotube 30a rigidly in place.

In another example embodiment of the present invention, the substrate is heated to about 300 degrees Celsius in air after the metal covers are deposited, and Ohmic electrical connection to the ends of the nanotube 30a are formed. Metal lines, such as line 33 in FIG. 6, can then be connected to the metal covers to provide macroscopic electrical connection to the nanotube 30a.

FIGs. 8A-8C show metal covers, such as those shown in FIG. 7, being made using lithographical patterning, according to another example embodiment of the present invention. Referring to FIG. 8A, a layer of spin-on resist 60 is deposited on top of catalyst islands 29 and nanotube 30a. In FIG. 8B, the resist 60 is etched in regions 61 where the metal covers 34 are to be located. A layer of metal is then deposited over the resist 60 and catalyst 29 (*e.g.*, by physical vapor deposition or CVD). The resist 60 is removed in a lift-off process in FIG. 8C, leaving the metal covers 34.

In another example embodiment of the present invention, FIG. 9 shows a side view of a device including a freestanding nanotube 30b capable of acting as a high-Q

resonator. The nanotube 30b is disposed above a surface 36 of an etched trench region 35 in the substrate 22 between catalyst islands 29 and is supported at ends 39 of the nanotube. In one implementation, the trench 35 and metal covers 34 are combined in the same apparatus.

The structure in FIG. 9 is useful in a variety of applications. In one example embodiment, the nanotube 30b is resonated by applying a magnetic field thereto (*e.g.*, perpendicular to the length of the nanotube 30b) and passing an oscillating current through the nanotube. A conductive film 37 is capacitively coupled with the nanotube 30b and extracts a resonant signal from the nanotube. In another implementation, the conductive film 37 is used to electrostatically excite mechanical vibrations in the nanotube 30b.

FIG. 10 shows a top view of a substrate 22 and islands 29, which can be used to make a nanotube structure as shown, for example, in FIG. 9. First, a nanotube 30b that connects catalyst islands 29 is grown. Other nanotubes may also be grown from both islands, but are not shown for clarity. Then, the substrate is masked with a resist, such as a spin-on resist, leaving an unmasked region defined by a box 38. Next, the region inside the box 38 is exposed to an etchant that removes substrate material without necessarily affecting the nanotube 30b. The etchant includes one or more of a variety of etchants, depending upon the composition of the substrate. For example, hydrofluoric acid can be used to etch SiO_2 or silicon substrates. Substrate below the nanotube 30b is etched, resulting in the nanotube being supported only at its ends 39 as shown in FIG. 9. Metal lines 33 are used to provide macroscopic electrical connections to the nanotube 30b via the catalyst islands 29. Metal covers, such as covers 34 in FIG. 8C, can be

deposited before or after etching the trench 35 to provide Ohmic electrical connections to the nanotube and improved mechanical stability for the nanotube ends 39.

FIGs. 11A and 11B show a suspended carbon nanotube being manufactured, such as the nanotube shown in FIG. 9, according to another example embodiment of the present invention. In FIG. 11A, a substrate 22 is etched to form the trench 35 where a nanotube is to be suspended. In FIG. 11B, islands 29 are disposed on opposite sides of the trench 35 and a nanotube 30b is grown from the islands 29 and electrically connects the islands. The distance across the etched substrate, and thus between the islands 20, is selected for the characteristics of a particular application, including manufacturing conditions and materials used. In connection with an example embodiment of the present invention, it has been discovered that using catalyst islands having a width of at least 1 micron and spacing the islands at a distance that is less than about 10 microns apart is particularly useful in forming carbon nanotubes extending between the two catalyst islands. In addition, if a number of catalyst islands are spaced at varied distances in an array, the likelihood of growing a carbon nanotube between islands is improved. As in the example embodiments above, one of the islands can be replaced with a metal pad, wherein the nanotube grows from the island 29 to the pad. In addition, metal covers, such as covers 34 in FIG. 8C, can be deposited on top of the nanotube 30b and catalyst islands 29.

In another example embodiment of the present invention (not shown), the nanotube 30b is freestanding, such that the nanotube is supported on only one end by a catalyst island 29 (*e.g.*, the freestanding nanotube does not extend all the way across the

trench 35). In this implementation, the nanotube is a cantilever and is adapted to be used as a resonator.

FIG. 12 shows a catalyst particle 45 located on a tip 47 of an atomic force microscope (AFM) cantilever 42, according to another example embodiment of the present invention. The cantilever 42 is supported by a base 49 and has a free end 48 opposite the base 49. The particle 45 may be made of one or more of a variety of catalyst materials, such as Fe_2O_3 (decomposed from $Fe(NO_3)_3$) and others, as discussed above. The catalyst particle 45 may or may not have supporting nanoparticles (*e.g.*, silica or alumina particles), and is firmly attached to the tip 47. Atomically sharp nanotubes 30 are grown from the particle 45, are firmly attached to the cantilever and are useful as probe tips for AFM. In one implementation (not shown), the cantilever does not have a tip 47 and the particle is disposed directly on the cantilever 42.

FIGs. 13A - 13D show a carbon nanotube on a tip being manufactured, according to another example embodiment of the present invention. In FIG. 13A, a substrate 50 is coated with a gold film 52, and droplets of $Fe(NO_3)_3$ dissolved in methanol are deposited on the gold surface. The methanol is then evaporated, leaving only small particles 54 of $Fe(NO_3)_3$ on the gold film 52. Next, an AFM tip 47 is brought into contact with a particle 54 of $Fe(NO_3)_3$ in FIG. 13B. An electric field is then applied between the tip 47 and the gold film 52. The electric field adheres the $Fe(NO_3)_3$ particle to the tip 47. In one implementation, the electric field also causes the $Fe(NO_3)_3$ to decompose into Fe_2O_3. In FIG. 13C, the cantilever 42 and tip 47 with the adhered $Fe(NO_3)_3$ particle 54 is removed from the gold film 52. The cantilever 42 and tip 47 are heated to fully decompose the $Fe(NO_3)_3$ particle 54 into an Fe_2O_3 particle 54

in FIG. 13D (*e.g.*, as shown in FIG. 12). Nanotubes 30 are then grown from the catalyst particle 45.

While the present invention has been described with reference to several particular example embodiments, those skilled in the art will recognize that many changes may be made thereto without departing from the spirit and scope of the present invention.